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1. Your reference

9049

2. Patent application number

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3. Full name, address and postcode of the or of
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Patents ADP number (*if you know it*)If the applicant is a corporate body, give the
country/state of its incorporation

4. Title of the invention

REDUCTION IN SOLIDS DEPOSITION

5. Name of your agent (*if you have one*)

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709343800

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Description 23

Claim(s) -

Abstract -

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Statement of inventorship and right to grant of a patent (*Patents Form 7/77*)

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11.

I/We request the grant of a patent on the basis of this application.

Signature F. M. Collins
COLLINS, Frances Mary

Date 21.6.99

12. Name and daytime telephone number of person to contact in the United Kingdom

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REDUCTION IN SOLIDS DEPOSITION

This invention relates to methods of reducing deposition of solids in particular from supersaturated solutions, and especially concerns reducing scaling.

Water often contains inorganic salts, in particular those of calcium and/or barium which may be of sparing solubility in water and tend to deposit on the inside walls of pipes, and in valves and tanks and on heat exchangers as scale. If scale is allowed to build up, it causes increased pressure losses, reduction in flow rate in pipes or heat exchange capacity and ultimately pipe blockage. Traditionally scaling problems are overcome by addition of scale inhibitors, which are organic compounds which complex at least some of the metals. But these are expensive and contaminate the water. Many other methods have been tried among which are application of ultrasonic energy to heat exchangers to remove scale and in well bores of oil wells (see e.g. I.A.Beresnev and P.A.Johnson, Geophysics, Vol.59 No.6, June 1994 pp1000-1017). But addition of scale inhibitors is the main commercial route today for reducing scaling problems.

Other problems involving unwanted solids deposition include the deposition of wax on cooling waxy oils, such as diesel fuel, residual and crude oils, and the deposition of gas hydrates, which are crystalline complexes of water and gaseous hydrocarbons such as methane, on cooling in pipelines carrying gas and water, and optionally crude oil, such as gas pipelines and live crude oil pipelines. Deposition of solids in the lines reduces the flow rate and increases back pressure and ultimately causes pipe blockage. Traditionally large amounts of methanol are added to dissolve the hydrates, or special hydrate or wax inhibitors are added to stop the deposits forming.

A new method of reducing solids deposition has now been invented which is

economic in energy on a large scale, but does not need addition of contaminating additives.

The present invention provides a composition for reducing deposition of solids from a supersaturated solution onto a solid surface in contact with the supersaturated solution which composition comprises either (i) a dispersion of seed crystals of the solid in a solution of the solid or (ii) a dispersion of seed crystals of a compound isomorphous with the solid in a solution of the isomorphous solid.

The present invention also provides a method of reducing deposition of solids from a supersaturated solution onto a solid surface in contact with the supersaturated solution which method comprises:

- (a) forming a dispersion of either (i) seed crystals of the solid in a solution of the solid or (ii) seed crystals of a compound isomorphous with the solid in a solution of the isomorphous solid;
- (b) distributing said dispersion into either (i) a supersaturated solution of the solid or (ii) a precursor liquid of the supersaturated solution which precursor liquid is saturated with respect to the seeds, and in the case of (b)(ii) converting the precursor liquid into a supersaturated solution of the solid; and
- (c) contacting the treated supersaturated solution with the solid surface.

Without wishing to be bound by any theory, it is believed that the reduction in deposition of solids from a treated supersaturated solution onto a solid surface is due to:
(i) the seed crystals reducing the average crystal size of the solid which crystallises out of the supersaturated solution so that the crystals are less likely to cause blockages;
(ii) the seed crystals accelerating the rate at which the solid precipitates out of the supersaturated solution i.e. the solution is supersaturated for a shorter period of time.
The contact time between the solid surface and the supersaturated solution is thereby reduced and consequently the solid is less likely to add to crystals which have formed on the solid surface; and
(iii) modification of the surface charge on the seed crystals.

The solids which would otherwise be deposited may be mineral salts, e.g. scaling salts, such as the carbonates and/or sulphates of alkaline earth metals, such as calcium, strontium, barium, or magnesium carbonate, or may be organic such as hydrocarbon waxes, e.g. from the oils as mentioned above, especially of 20-80 carbons, and hydrates

of alkanes of 1-3 carbons, e.g. methane, ethane or propane or mixtures thereof. The mineral salts are found in aqueous liquids and waxes in organic liquids and the hydrates may be in aqueous or organic liquids or mixtures of both.

The solid seeds may be in a saturated solution, which for mineral salts in water
5 may contain up to 3000 ppm of the salt in question such as 100 up to 2000 ppm for barium sulphate and 20 up to 700 ppm for calcium carbonate. Alternatively, the solid seeds may be in a solution which is below the thermodynamic solubility limit of the mineral salt.

For waxes in oils the saturated solution may contain 1-15% by weight, for
10 example 5-10% by weight of said wax (i.e. the one(s) which forms the seeds). The saturated solution of a methane hydrate in water can contain at least 80% by weight, preferably 80-90% by weight, for example 85% by weight of water.

The seed crystals may be of Mean particle size 0.1 - 5 microns, in particular 0.5 -
2 microns, preferably 0.5 - 1.5 microns for mineral salts (the crystals having at least 2
15 dimensions within this range), and 0.5 - 50 microns for the waxes and 0.1 - 20 microns
for the gas hydrates.

The seed crystals usually have 0.01-0.8, for example 0.025-0.5 times the average
diameter of crystals of the same solid, which have been allowed to crystallise out from a
supersaturated solution thereof on standing and without any outside influences apart
20 from gravity and time.

The seed crystals have no live growing surfaces and therefore in their dispersion
in the saturated solution will not grow bigger on standing other than by Ostwald ripening
in which small particles dissolve and large particles grow. However they are still capable
of growing if placed in a supersaturated solution.

The seed crystals are usually of the same compound whose deposition on the
surface is to be altered, but may be of a compound isomorphous therewith; thus for
example calcium or magnesium carbonate seeds may be used to alter the deposition of
strontium carbonate, while wax seed crystals of primarily 20-30 carbons may be used to
alter the deposition of waxes primarily of 40-60 carbons.

30 The form of the seed crystals may also be different in crystal morphology or habit
from those which would otherwise naturally form from the supersaturated solution.
Thus where the deposited solid can exist in 2 or more crystalline forms, which differ in

morphology i.e. the compound is polymorphic, and the form naturally deposited from the supersaturated solution is of one form, then the seed crystals should preferably be in a different crystalline form. The seed crystals are preferably of the more thermodynamically stable polymorph. Thus calcium carbonate has 3 crystalline forms, of which calcite is deposited slowly from supersaturated solution, but aragonite is deposited rapidly; in this case the seed crystals used should preferably be of the latter form. In the case of barium sulphate, as explained below, the slowly made normal form is generally star shaped e.g. with 8 point rosettes (with one dimension thickness less than 0.4 times of each of the other dimensions) or distorted rhomboid, while the rapidly made form is rectangular, oval or undistorted rhomboid, usually with voids, with one of its 3 dimensions of a length 0.4-1.5 times that of the other dimensions, especially with the dimensions in the ratio 1-1.5:1:0.4-0.8. More details are provided hereinafter in respect of barium sulphate.

The seed crystals may be made separately from the solution in which they are dispersed, so they may be made, isolated from their production medium, and then dispersed in the solution. Preferably they are made in that solution and used as such as the dispersion, or the dispersion produced may be concentrated e.g. by centrifuging or via a cyclone to increase the insoluble solids content of the dispersion. The seed crystals are usually present in the dispersion in weight amounts of 1-60%, e.g. 10-40% (based on the total weight of dispersion).

The seed crystals may be made by rapid crystallisation from a solution at least partly over saturation concentration with respect to the seed compound. The rapid crystallisation may be induced by rapid cooling, especially in the presence of a seed growth initiator location, such as a residual seed from a previous operation or a scratched surface, e.g. on an agitator or vessel, pipe, valve, or other bare metal surface. Rapid crystallisation may also be achieved from a saturated solution by addition of a non solvent for the solid to be deposited which is miscible with the saturated solution e.g. an alcohol such as methanol or ethanol in the case of mineral salts, or an aromatic hydrocarbon such as toluene or xylene in the case of hydrocarbon waxes.

Preferably however the seed crystals are obtained via physical disturbance of a supersaturated solution before significant nucleation starts. In the case of solutions in which such nucleation proceeds slowly (e.g. after cooling wax solutions or reducing the

pressure or temperature of gas/water mixtures), the disturbance may be directly on the solution after its production, but in the case of solutions in which nucleation proceeds fast, the disturbance is usually at the location of its production. Thus, when a supersaturated solution is made by mixing solutions of 2 or more components or ingredients, then the disturbance is usually at or near the location of mixing. The disturbance may be to one or more of the solutions which are to be mixed provided that the disturbance is near the location of mixing.

The physical disturbance may be generated in many different ways, for example by mechanical vibration or stirring, oscillation or rotation, enhancement of natural convection, electric fields, magnetic or electromagnetic stirring, detonation and shock waves, vortices (however produced), agitating with gas bubbles, release of pressure, etc. Generation of cavitation in the solution is preferred. This cavitation may also be achieved using hydrodynamic means such as a propeller or lifting surface so as to create vortices in the liquid. The preferred form of the disturbance is sonic or ultrasonic vibration, most preferably ultrasonic.

Ultrasound may be applied to the solution as soon as physical conditions allow it to become supersaturated or (supercooled), and preferably before any spontaneous nucleation may occur. If desired more than one method of effecting the disturbance may be used, especially ultrasonic vibration and a mechanical method e.g. hydrodynamic or mechanical agitation.

Small bubbles of the vapour phase or dissolved gas form out of a liquid as a wave of physical disturbance passes through the solution. These bubbles collapse after the wave has passed, causing a large pressure change which in turn induces nucleation in the liquid.

The preferred frequency of the ultrasound is 16-100kHz. Above 100kHz little nucleation can be obtained except at extremely high power. The particularly preferred frequency is between 16 and 40kHz. Energy densities of 0.1 - 1000 J/cm³, for example 1 - 100 J/cm³ are preferred, especially at the latter frequencies.

The duration of applied ultrasound is usually 0.05-360 sec. The application of ultrasound to a supersaturated (or supercooled) solution can result in the formation of many nucleation sites, resulting in small crystals which are desired in the invention. In liquids where crystals exist, either formed 'spontaneously' or by applied physical

disturbance, new crystals may be formed by fragmentation either due to cavitation or other effects induced by the ultrasound, such as acoustic streaming. This phenomenon is referred to as grain refinement or grain multiplication. Crystals formed in an ultrasonic field may also be found to have different surface properties (charge etc.) which modify 5 their subsequent adhesion properties as described below with respect to barium sulphate.

For many applications the use of ultrasound will modify simultaneously both nucleation and crystal growth. However, these two phenomena may be controlled independently in the invention by applying the disturbance at appropriate different stages of the solidification process, especially from super cooled solutions from which solid 10 deposits slowly. Generally, the ultrasound may be applied to the solution either before or during the solidification process or following storage.

Ultrasonic vibrations may be generated by a convenient means, in particular using electromagnetic, piezoelectric, electrostrictive or magnetostrictive devices, piezo electric ones giving low power per unit volume of solution contacted and acoustic horns giving 15 high power per unit volume. The ultrasonic power and frequency required will, in part, be determined by the viscosity, temperature (e.g. 0-100°C) pressure (0.1-10 Bar), presence of solids, immiscible liquids and gas bubbles, dissolved gas content etc. of the fluid to be treated. In general, the desired ultrasonic conditions are those which result in cavitation in the bulk supercooled or supersaturated liquid to induce nucleation or to 20 cause grain refinement. High intensity ultrasound may be generated most readily at the lower ultrasound frequencies, such as 20 kHz.

The efficiency of nucleation in a fluid will be dependent on the extent of supersaturation or supercooling, and the density and distribution of the cavitation sites within the fluid. The degree of supersaturation over the saturation level may be 1.1-5 25 times e.g. 1.5-2 times over that level, especially for slow crystallizers such as waxes or hydrates or 1.1-1000 e.g. 20-500, preferably 50-400 times over the level for fast crystallizers such as mineral salts.

The sources of ultrasound may be coupled directly to the solution but may also be connected indirectly via coupling mechanisms such as horns, waveguides and/or 30 through the walls of the container holding the liquid, or walls of the pipe line through which it passes.

In a preferred process for making the seed crystals a supersaturated solution e.g.

of mineral salts such as barium or calcium carbonate or sulphate is produced by passing 2 or more solutions of the separate components e.g. barium or calcium chloride and sodium sulphate or carbonate to a locus of mixing, at which the supersaturated solution is made in situ and the physical disturbance e.g. ultrasonic treatment is applied. There 5 result small seed crystals of the solid and after sufficient time e.g. 0.1-10 secs, the crystals grow until the supersaturation level is either reduced to saturation level in which case a suspension of seed crystals in a saturated solution is made or to below the thermodynamic solubility limit of the solid in which case a suspension of seed crystals in a solution of the solid is made. The physical disturbance e.g. ultrasonic treatment may be 10 applied throughout this time to the supersaturated solution until the desired suspension is made, but preferably it is applied only to the locus of mixing and then the seed crystals allowed to grow to reduce the degree of supersaturation. The amount of crystals of the solid produced is usually 1-60% w/w of the total weight of crystals and solution produced at the locus of mixing.

15 In order to increase the contact time for the turbulence to take effect to produce a dispersion of seed crystals, the flow rate of supersaturated solution passing under the influence of the turbulence may be reduced e.g. to give a power per unit volume of solution treated per sec of 0.1 - 1 W per cm³ per second. The flow rate may be less than that of the source of the supersaturated solution (or precursor liquid and complementary 20 ion liquid). Thus to reduce the flow rate, the diameter of the input line may be reduced or an impeller may be present in the line to slow liquid flow down and ideally to transmit the power gained to one or both of an agitator at the location of seed crystal generation and a propeller for use in a pump to accelerate the flow rate of the product suspension of seed crystals for mixing with the supersaturated solution or precursor liquid.

25 The dispersion of seed crystals is then mixed with the supersaturated solution, in the case when the rate of crystal growth is normally slow, or with a precursor liquid used to make the supersaturated solution, in the case when the rate of crystal growth is normally fast; the precursor liquid is inert to the crystals, as is a solution of the solid. Thus in the case of waxes or gas hydrates, the mixing of the crystal suspension may be 30 with a supersaturated wax solution or water/gas mixture or may be with a saturated solution of the wax or hydrate, before reduction in temperature or pressure (at which time crystals would deposit in the absence of seeds). For mineral salt seeds, the mixing

may be with a precursor liquid containing at least one of the salt ions, which precursor liquid is saturated with respect of the seeds; thus the seed suspension of barium sulphate may be added to a solution comprising barium chloride (or sodium sulphate) saturated in barium sulphate e.g. high barium formation water or sea water respectively. The 5 precursor liquid (with suspension) may then be altered to produce supersaturated solution, e.g. by change of temperature (for wax or calcium carbonate), pressure (gas hydrate or calcium carbonate) or mixing with a solution comprising the complementary ions e.g. sea water containing sodium sulphate (or formation water comprising barium chloride respectively). If desired the dispersion of seeds may be co-mixed with both the 10 precursor liquid and the solution with complementary ions.

The dispersion of seed crystals is mixed with the supersaturated solution under conditions of turbulence e.g. with a Reynolds Number of at least 2000 e.g. 3000 - 4000 while the mixing with precursor liquid may or may not be under turbulent conditions. The mixing may be achieved with mixers, with or without moving parts. The former 15 include mixers with paddle wheel or other stirrers, while the latter include jet and venturi mixers and other devices in which a small stream of fluid (here dispersion) is passed into a flowing stream of a second fluid at or upstream of a point of maximum turbulence.

The percentage weight of seed crystals from the dispersion to total weight of seed crystals and depositable solids in the supersaturated solution is generally in the 20 range 1 - 75% w/w e.g. 10 - 60% w/w, more preferably 10 - 50% w/w. The depositable solids are those which would otherwise deposit downstream of the mixing zone in the absence of the seeds i.e. relates to the degree of supersaturation. Thus, if the precursor solution is of wax and the temperature is to be reduced, then the relative weight is in respect of the seeds and total of seeds and wax crystals otherwise separating at the 25 reduced temperature.

In the case where the seed dispersion is mixed with a precursor liquid prior to addition of a second component resulting in deposition e.g. in the case of mineral salts, which crystallise fast from supersaturated solution such as barium sulphate or calcium carbonate, the percentage weight of seed crystals to the total weight of seed crystals and 30 depositable solids is usually as given above.

If desired, especially when the relative weight of the dispersion to the total weight of supersaturated solution that has to be converted to saturated solution (e.g. to

be stopped from causing scaling, is low (e.g. 5-20%), the mixing of the seed dispersion and the supersaturated solution (or precursor liquid) may be performed at least twice e.g. 2-4 times with at each stage the above volumes of seed dispersion to total volume of dispersion and supersaturated solution. Thus a 40% w/w seed dispersion may be added 5 in a 1:3 weight ratio to the supersaturated solution (or precursor liquid, prior to effecting supersaturation) to produce a second dispersion of 5-20% w/w crystals in a saturated solution; this second dispersion, preferably after concentration to 30-50% solids, may then be mixed with fresh supersaturated solution or precursor liquid as described and a 10 third dispersion in saturated solution produced. This process can be repeated several times, until all the original supersaturated solution or precursor liquid has been treated. In each stage the product is a dispersion of crystals in a saturated solution, before addition of more supersaturated solution or precursor liquid.

If desired, the dispersion of crystals may be divided and the divided dispersion used to treat separate portions of the supersaturated solution or precursor liquid. Thus 15 the multi step mixing of the seed dispersion and the supersaturated solution or precursor liquid (prior to effecting supersaturation) may be performed in steps in series or in parallel or a combination of both.

In its simplest form, particularly with compounds that crystallise slowly, the seed dispersion is mixed with the supersaturated solution to effect crystallisation to produce a 20 dispersion of solid in saturated solution. When the seed dispersion is mixed with precursor liquid, then, after mixing, the physical or chemical conditions may be changed to generate the supersaturated solution at least incipiently and then the crystallisation may start. Thus the physical condition changed may be temperature (e.g. cooling) or pressure (e.g. reduction) while the chemical conditions may be addition of a precipitating 25 component, e.g. a complementary ion e.g. sulphate ion for mineral salts, or non solvent.

After the mixing of the seed dispersion and the supersaturated solution, crystallization is allowed to occur eventually to produce a slurry of crystals in a saturated solution with reduced deposition on walls of solid surfaces in contact therewith. It is believed that the form of crystals produced is of different adhesive properties to those 30 made without the influences of the physical disturbance and that the contact time between the supersaturated solution and the solid surface in contact therewith is reduced.

The present invention also provides an apparatus for effecting controlled solid

deposition, which comprises:

a crystal seed generator chamber, having an inlet for a supersaturated solution or a first inlet for a first precursor liquid of the supersaturated solution and a second inlet for a second precursor liquid of the supersaturated solution, a means for creating turbulence

5 e.g. cavitation in a solution in said chamber to effect crystallisation, and an outlet for a dispersion of seed crystals, a line for said dispersion leading from said first chamber to a second chamber which second chamber has a first inlet for said dispersion, a second inlet for a supersaturated solution or precursor liquid thereof, a mixing means, and an outlet.

The crystal seed generator chamber may have a plurality of means for creating

10 turbulence each of the means acting on different zones of the chamber. Alternatively, the apparatus may contain a number of crystal seed generator chambers connected in series, for example 2 - 4, preferably 2 - 3 crystal seed generator chambers.

When the second inlet is for a supersaturated solution of a solid the outlet from the second chamber is for a dispersion of seed crystals in a solution of the solid. When 15 the second inlet is for precursor liquid, the apparatus also, preferably provides means for effecting a change in physical or chemical condition of the blend of precursor liquid and seed dispersion, said means being applied to said second chamber, or to a third chamber attached by a line to said outlet from said second chamber. Said means may comprise a cooling means e.g. a heat exchanger, or pressure reduction means e.g. a valve, or an inlet 20 for a precipitating component e.g. complementary ion. Said means may also be located upstream of the second chamber to deliver a supersaturated solution to it e.g. in a line joined to said second inlet to the second chamber.

The supersaturated solution, which is to be treated in the process of the invention, may be divided into a small stream (e.g. 1-20% such as 5-10% of the total 25 volume) and a remaining stream, the small stream being submitted to the turbulence e.g. cavitation treatment to produce the seed dispersion, which dispersion is then re-mixed with the remaining stream (in one or more steps). Thus, the apparatus can comprise a first line for the supersaturated solution, at least one side line therefrom forming a loop from the first line and returning thereto at a second chamber, a first chamber spacing said 30 side line and comprising means for creating turbulence e.g. cavitation in the contents of said side line (i.e. of the loop) and said second chamber comprising mixing means.

When the seed dispersion is to treat a precursor liquid containing one component

of a depositable solid especially a rapidly depositing one, such as a mineral salt, prior to or simultaneously with addition of at least one other component, to form the combination of first and other components, the apparatus preferably comprises a first line for a solution of said first component (e.g. an alkaline earth metal) saturated with the

5 depositable solid (e.g. an alkaline earth metal carbonate or sulphate), a side line therefrom forming a loop and returning to said first line at a second mixing location which is in a second chamber, a first chamber comprising said turbulence creating means in said loop at a first mixing location in said first chamber and first inlet at said first location for at least one other component of said depositable solid, and a second line and

10 second inlet for said second component into said second mixing chamber. Preferably the first and second inlets for the second component are joined by a third line; advantageously the apparatus has a fourth line for the second component, said fourth line having a side line leading to said first inlet and the rest of the fourth line leading to the second inlet.

15 Thus, preferably the apparatus comprises said first and second lines, meeting at a second mixing location, side lines from each of the first and second lines which side lines meet at a first mixing location, means for creating turbulence e.g. cavitation at said first mixing location and an exit line from said second mixing location to said second mixing location.

20 If desired, there may be 2 first lines, one to each of the first and second chambers, and 2 second lines, one to each of the first and second chambers, the first lines being separate from each other, and the second lines being separate from each other. Also, if desired, the outlet from said first chamber may be linked to said second line spaced from said second chamber.

25 In the event that the solution of the first component contains sufficient of the first component that the suspension leaving the second mixing location still contains enough first component to effect more solidification with the solution of the second component, the second line may extend to lead to a third mixing location where it meets the exit line from the second mixing location. This disposition of lines may be repeated one or more times, to effect multi-step series addition of the second component, (e.g. sodium sulphate solution such as sea water) to a first component e.g. barium chloride solution such as formation water.

Preferably, the apparatus of the present invention includes a means for monitoring the size of the crystals. Alternatively, a separate apparatus may be provided to monitor the size of the crystals. This allows any failure or malfunction of the apparatus of the present invention to be detected before solid can build up on the solid surface.

The invention is particularly applicable to the reduction of mineral salt e.g. barium sulphate scaling.

Underground formation water can contain barium (e.g. at a level of up to 3000 ppm, for example 50-500 or about 250 ppm) and usually also calcium (e.g. at a level of up to 30,000 ppm, for example 1000-5000 ppm, such as 2500 ppm) both in the form of soluble chlorides, but also in the presence of sulphate ions, so the water is saturated with barium sulphate, and usually also calcium sulphate. This formation water can meet another aqueous composition e.g. sea water, which can contain soluble carbonate (e.g. at 100 - 5000 ppm) and/or sulphate (e.g. at 1000 - 3500 ppm); the other composition may also be a formation water from a different formation e.g. different strata level. Mixing the two waters produces a supersaturated solution of barium sulphate and/or carbonate, and/or calcium sulphate and/or carbonate, from which scale comprising these compounds deposits on surfaces. The meeting can be in the formation, when sea water is used as a secondary injection liquid injected at a distance from a production well to increase its production rate, (i.e. a water flood treatment). The scaling may occur in the formation or at locations downstream thereof in the production well pipeline or downstream thereof (especially if different formation waters meet there), or downstream thereof e.g. in the well head lines, or gas/liquid separator (for separating oil/water liquid from gas) or downstream thereof, (especially when live crude oils with different formation waters are passed to the same separator) or in any transport pipeline leaving the separator or the well head carrying the crude oil or produced water or both or especially in any production water pipeline downstream of any separator for separating crude oil from production water, in particular when different production waters have been mixed. The carbonate scale may also form in the gas/liquid separator or downstream thereof, due to reduction in gas pressure causing soluble calcium bicarbonate to form insoluble calcium carbonate. The treatment of the invention can be applied upstream of the above locations where scaling would otherwise happen. Particularly the treatment is applied

when two or more formation waters or production waters meet, or either or both meet sea water; such mixings are otherwise desirable when the waters especially production waters from more than one source are to be reinjected downhole via a single line. The treatment is especially applied between a produced water separator and such a

5 comingling location prior to a single reinjection well.

As explained above, the barium sulphate seed crystals used in the process of the invention are usually in a crystalline form, which is rectangular, oval, or undistorted rhomboid and preferably has voids, rather than the more conventional star shape or distorted rhomboid shape.

10 The present invention provides barium sulphate crystals having 3 dimensional distances of length, breadth and thickness, normal to one another, and one of which is 0.4-1.5 times the dimensional distance of the other, especially with the dimensions in a ratio of 0.4-1.5:1:0.4-1.5, such as 1-1.5:1:0.4-0.8. Preferably, the crystals have one or more voids therein e.g. 1-4, but especially 1 void. The voids are usually open on at least

15 one side to the envelope of the outer surface of the crystals, rather than being wholly enclosed. The voids preferably occupy 5-40% e.g. 10-30% of the volume enclosed by the envelope of the outer surface of the crystals. By envelope is meant the outer delimiting surface of the crystals. The crystals may be rectangular in at least 2 dimensions, especially cuboid. The voids may have linear or curved inner faces,

20 especially curved faces, so the crystals are preferably rectangular with 1 or 2 voids having curved inner faces. Angular crystals tend to be made from highly supersaturated solutions with low turbulence treatment times e.g. 0.5 to 5 sec. The crystals may also be ovoid, with an ellipsoidal envelope, but again preferably have one or more voids, such as those described above; these may be made from highly supersaturated solutions with high

25 turbulence treatment times e.g. 5 - 30 sec. The crystals may also be rhomboid in which case the crystals may have two flattened corners and two pointed corners. Rhomboid crystals tend to have dimensions in a ratio of 0.4-0.6:0.9-1.1:0.9-1.1, for example, 0.5:1:1 (thickness : length : width).

The barium sulphate crystals are usually substantially free from any barium or

30 sulphate containing liquid and hence are usually isolated solids. Their particle sizes are usually as described above. The particle size distribution is usually within at least one of the following; at least 35% of not more than 1 micron, at least 50% of not more than 1.5

micron and at least 60% of not more than 2 micron.

The barium sulphate crystals are usually made as described generally above, but especially by physically distributing e.g. cavitating a supersaturated aqueous solution containing barium and sulphate ion before significant nucleation starts, i.e. starting this distribution in the substantial absence of preformed crystals of barium sulphate different morphologically from those of the invention. The crystals of the invention are preferably made by application of ultrasonic vibrations to the supersaturated solution, especially at a location where separate flows of solutions comprising barium and sulphate ions meet.

5 The conditions of the ultrasonic treatment are usually as generally described above, with short treatment times giving the rectangular crystals with voids, and long treatment times giving ovoid crystals often with voids. The process provides a suspension of crystals in a 10 solution of barium sulphate, from which the crystals can be isolated if desired by filtration.

When the barium sulphate seed crystals having voids are used to seed a 15 supersaturated solution of barium sulphate (or precursor liquid therefor), it has been found that, in the produced barium sulphate crystals, the voids are smaller or substantially absent, with the voids from the seeds being at least partly filled with the 20 fresh barium sulphate deposited from the solution or liquid.

The present invention also provides rounded calcium carbonate crystals. 25 Preferably, the calcium carbonate crystals have a diameter in the range of 1 to 4 microns, preferably 1.5 to 2.5 microns, for example 2 microns. The calcium carbonate crystals are usually made as described generally above, but especially by physically distributing e.g. cavitating a supersaturated aqueous solution contain calcium and carbonate or bicarbonate ions before significant nucleation starts (as for barium sulphate).

Without wishing to be bound by any theory, it is believed that the seed crystals 30 used in the process of the present invention are more effective at growing crystals in the body of a supersaturated solution rather than allowing deposition on neighbouring surfaces, compared to processes with other kinds of seed crystals added in a different way. It is also believed that the seed crystals act by accelerating the rate at which solid precipitates from solution.

The barium sulphate seed crystals are especially suitable for decreasing barium sulphate scaling.

The invention is illustrated with reference to the following drawings in which Figures 1 to 3 are schematic flow diagrams of the process of the invention. Figures 4 to 6 are Scanning Electron Micrographs (SEMs) of barium sulphate crystals and Figures 7 and 8 are Scanning Electron Micrographs of calcium carbonate crystals.

Referring now to Fig. 1, line 1 has a inlet line 2 leading to an inlet 3 to a chamber 4, having applicable to at least part of its contents turbulence generator 5 e.g. a cavitation generator, and especially an ultrasonic resonator. Chamber 4 has an outlet 13 for a slurry of the seed crystals leading via a slurry line 6 to a chamber 11 fitted with a mixer 14. Chamber 11 has an inlet 16 joined to slurry line 6, an inlet 17 joined to input line 18 and an outlet 19 leading to product line 12. In use, a supersaturated solution of a depositable solid passes in line 1 via line 2 to chamber 4 where it is rendered turbulent by generator 5 to produce a slurry of seed crystals of the solid. The slurry passes in line 6 to chamber 11 where it mixes with supersaturated solution entering from line 18 and effects crystallisation thereafter before the supersaturated solution reaches a locus of deposition (not shown) where solid would otherwise have deposited if the turbulence generator had not been used. This procedure is of particular value when the rate of deposition of solids from the supersaturated solution is slow, or the degree of supersaturation is small. Line 18 may include a producer for increasing the degree of supersaturation of the supersaturated solution (not shown) which producer may be a cooler (for wax) or pressure reducer (for calcium carbonate) to deliver a higher supersaturated solution for meeting the slurry from line 6. Chamber 4 may also comprise such a producer, though it may be present in line 2 (not shown) to create a supersaturated solution in chamber 4. Thus, if desired the liquid in line 1 upstream of line 2 or in line 18 may be saturated or even less than saturated in the depositable solid, so long as there is such a producer upstream or at of each of chambers 4 and 11. When as shown, lines 1 and 18 are separate, there are different lines for supersaturated solution passing to chambers 4 and 11, so, the solution passing to chambers 4 and 11 may be different, though of the same components, e.g. at different concentrations. Preferably, (as shown dotted in Fig 1) lines 1 and 18 are joined so the same supersaturated solution passes to both chambers, and lines 2 and 6 constitute a side line or loop on line 1.

In Fig.2, comparable lines to those in Fig.1 have the same designation, so feed line 1 has an inlet line 2 and slurry line 6 spaced by chamber 4 with turbulence generator

5 e.g. cavitator especially ultrasonic generator. Chamber 4 has an extra inlet 7, joined to feed line 8, which leads from feed line 9. Line 10 and slurry line 6 meet an input line 18 at chamber 11 which also contains mixer 14 and, from which a product line 12 leaves.

As described with respect to Fig 1, lines 1 and 18 are preferably joined (shown dotted in

5 Fig 2) and lines 9 and 10 are preferably joined (shown dotted in Fig 2). In use, a first solution of one component of a depositable solid, which is a saturated solution thereof (e.g. formation water of significant barium ion concentration in a saturated barium sulphate solution) passes in line 1 and then via line 2 chamber 4. A second solution of a second component of the depositable solid (e.g. sea water containing sulphate ion)

10 passes in line 9 in to line 8 to chamber 4. The first and second solutions meet in chamber 4 under conditions of turbulence from generator 5, to produce a slurry of seed crystals e.g. of barium sulphate. The slurry leaves chamber 4 via outlet 13 and line 6 to enter chamber 11, where it meets more first and second solutions entering from lines 1 and 10 respectively and mixed by mixer 14. In the chamber 11, there is strong agitation of the supersaturated solution produced from first and second solutions, in the presence of the seed crystals from line 6. Crystallisation occurs in the liquid to give solid having a reduced tendency to deposit on surfaces. The mixture of solid and saturated solution passes in product line 12 through the zone of deposition downstream, (not shown) where solid would otherwise have deposited. This apparatus is especially suitable when the rate

15 of solid deposition from the supersaturated solution would be high if features 2-19 were absent. It is suited where supersaturation very rapidly occurs from the mixing of 2 solutions e.g. barium sulphate supersaturated solution resulting from mixing of sea water and barium ion containing formation water.

20

If desired (not shown) a stepwise crystallisation from line 1 in Fig.2 may be used

25 with one or more further chambers 11A, 11B etc. downstream in line 12 and one or more successive feed lines 10A, 10B etc. from line 10 into the further chambers 11A, 11B etc. (not shown)

As with Fig 1, the lines 1 and 18 to chamber 4 and 11 may be for containing different solutions, e.g. different formation or production. Waters or different sea waters

30 and likewise the lines 8 and 10 to chambers 4 and 11 may also be for containing different solutions e.g. different sea waters (not shown). When lines 1 and 18 are joined and 9 and 10 are joined, the same solutions can be used to

provide both first solutions and second solutions respectively.

Fig 3, shows a modification of the apparatus shown in Fig 2 in which the line 6 does not join chambers 4 and 11 but rather joins chamber 4 to line 10 at location 15. In use the slurry of crystals leaving chamber 4 is passed to line 10 at location 15 where it is 5 diluted by the second component solution (e.g. sodium sulphate solution, such as sea water) and the diluted slurry produced is passed to chamber 11. In this way the seed crystals are more easily distributed in chamber 11 with the supersaturated solution for precursor liquid from line 1, because they have already been partly distributed in one of the other liquids feeding chamber.

10 Fig. 4 is an SEM photograph of seed crystals of barium sulphate having voids, produced using ultrasound.

Fig. 5 is an SEM photograph of seed crystals of barium sulphate which have been used to seed a supersaturated solution of barium sulphate in which the voids have been at least partially filled with barium sulphate deposited from the supersaturated solution.

15 Fig. 6 is an SEM photograph of crystals of barium sulphate which were allowed to crystallise out of a saturated solution without any outside influences apart from gravity and time.

20 Fig. 7 is an SEM photograph of seed crystals of calcium carbonate which were allowed to crystallise out of a saturated solution without any outside influences apart from gravity and time.

Fig. 8 is an SEM photograph of crystals of calcium carbonate produced using ultrasound.

The invention is illustrated in the following Examples.

Example 1

25 The apparatus as illustrated in Fig 2 was used with lines 1 and 18 joined and 9 and 10 joined, with flow rates of 0.05 ml/min of Formation Water (FW) in line 2, 4.95 ml/min of FW entering chamber 11 from line 18, 0.05 ml/min of Sea Water (SW) in line 8 and 4.95 ml/min of SW entering chamber 11 in line 10, and 0.1 ml/min of seed crystal suspension entering chamber 11 in line 6. A coil of stainless steel tube one sixteenth of 30 an inch (1.6mm) internal diameter was present in line 6 and another in line 12, both for liquid hold up purposes and a blockable tube downstream of the coil in line 12 was present to determine blocking pressures or

deposition rates. The lines 1, 2, 6, 8, 10 were all (one eighth inch (3.2 mm) 1D tube.

The Formation water in lines 2 and 10 contained:

NaCl (64.24g/L), NaHCO₃ (2.82g/L), CaCl₂.2H₂O(2.35g/L); KCl

(2.25g/L), BaCl₂.2H₂O(1.39g/L), MgCl₂.6H₂O(0.88g/L), SrCl₂.6H₂O (0.24g/L) in 1 litre

5 water and pH adjusted to 4.5 by dropwise addition of dilute hydrochloric acid or sodium hydroxide.

The Sea Water in lines 8 and 10 was at pH 4.5 and contained:

NaCl (23.97 g/l), NaHCO₃ (0.17 g/l), CaCl₂.2H₂O (1.57 g/l), KCl (0.87 g/l),

MgCl₂.6H₂O (11.11 g/l), SrCl₂.6H₂O (0.024 g/l), Na₂SO₄.10H₂O (9.93 g/l) in 1 litre of

10 water.

Chamber 4 had a mixer and ultrasonic horn 5 (maximum power of 5000J/cm³), at a frequency of 20 kHz at the points of mixing of the waters from lines 2 and 8.

Action of the ultrasound produced turbulent flow in the mixer in chamber 4 of Reynolds Number of at least 2000. Chamber 11 contained a T piece mixer for mixing 15 the streams from lines 6, 10 and 18, under conditions of turbulent flow.

The process was performed without use of the ultrasound generator 5 and then with ultrasound generator 5 which had been operated for 2 - 3 seconds to ensure equilibrium was reached. In each case slurry in the tube upstream of chamber 11, but downstream of the coil was analysed and the nature of the barium sulphate crystals in it 20 determined by Scanning Electron Microscopy and their particle size determined. The results were as follows; without ultrasound, Mean particle size 2.04 microns, Standard Deviation 2.01 microns No of particles per ml ($\times 10^6$)35, with ultrasound Mean particle size 1.03 microns, Standard Deviation 0.71 micron and No of particles/ml($\times 10^6$)159.

The slurry in line 6 at the time of entry to Chamber 11 contained 10 % by weight 25 barium sulphate crystals in a solution thereof. The crystals from use of ultrasound were substantially rectangular with larger curved voids extending inwardly from the surfaces, while those obtained without use of ultrasound were star shaped (see Attached SEM photographs Figures 4 and 6).

In addition, in a separate experiment without ultrasound, barium sulphate seeds 30 of 1.03 microns Mean particle size (generated upstream of the seed injection point in the ultrasound mixing chamber described above) were present in the Formation Water added to Chamber 11. The analysis of crystals downstream of chamber 13 showed mean size

2.58 microns, Standard Deviation 1.81 microns, No of particles/ml($\times 10^6$) 35.

The weight of crystals deposited in the coil tube downstream of chamber 11 (expressed as mg barium sulphate per l of solution passed) was also determined with time by measuring the concentration of eluted barium (in solution) using inductively coupled plasma spectroscopy (ICP). After 7 hours with no ultrasound about 60 mg/l of solid had been deposited, while in the experiments with ultrasound the deposits were 25-32 mg/l, and this level remained at least until 24 hours.

Example 2

The process of Example 1 with ultrasound was repeated with a lower ultrasound power input namely 1600 J/cm³. Similar results to those in Example 1 were obtained for the particle (crystal) size parameters.

Example 3

The process of Example 1 was repeated but with the apparatus of Fig. 3, with separate feed lines of formation water in lines 1 and 18 to chambers 4 and 11, and with separate feed lines of sea water in lines 8 and 10. In this way the effect of different relative flow rates of seed slurry in line 6 and formation water into chamber 11 was changed. The results were as follows. Flow rates in lines 1 and 6 were 2l/min., and 8.7l/min in each of the lines for formation and sea water into chamber 11. These give a percentage of seed slurry to total liquid in chamber 11 of 10% (by weight). Residence times were 3.1 sec from chamber 4 to location 15, 3.5 sec from, location 15 to chamber 11, and 3.8 sec from chamber 11 to the blockable tube. No blocking occurred. With the latter two residence times reduced to 2.1 sec and 1.2 sec respectively (and sea water and formation water flow rates of 8.5l/min each giving a 11% seed percentage) blocking occurred.

With different flow rates (namely 4l/min for formation and sea water, giving 20% seeding, and residence times (as above) of 3.1, 3.6 and 2.3 secs respectively, there was again no blocking (and no deposit in the blocking tube).

With different flow rates (namely 3l/min for formation and sea water) and 4l/min for seed crystal slurry, giving 40% seeding, and residence times (as above) of 1.5, 3.1 and 2.3 secs respectively, again there was no blocking and only 2 mg/l deposit in the blocking apparatus.

In each case the energy per unit volume of liquid in chamber 4 from resonator 5

was in the range of 5 - 80 J/cm³.

Example 4

The process of Example 3 was repeated with all the formation water and seawater mixed in chamber 4 to give a total flow rate of 6l/min and no addition of extra 5 in lines 10 and 8. The example was repeated with and without ultrasonic generation of turbulence. Without ultrasonics, the pressure in the blocking tube rose to 5.8 bar after passage of 50 litres of total water giving 340mg/l deposit, while with ultrasonics, the pressure was still substantially zero after 520 litres of water had been passed and only 13 mg/l of deposit had formed.

10 In related experiments performed at 20 l/min total volume and with and without ultrasonics, the average particle size of the solid produced after the mixing point was 1.05 microns with ultrasonics and 5.6 microns without ultrasonics.

Example 5

A formation water containing NaCl (74.1821 g/l), KCl (0.71 g/l), NaHCO₃ (0.68 g/l), 15 CaCl₂.2H₂O (10.3 g/l), MgCl₂.6H₂O (4.22 g/l), SrCl₂.6H₂O (1.75 g/l), BaCl₂.2H₂O (0.45 g/l) was rapidly mixed with seawater (500 ml; having the same composition as in Example 1) in an ultrasonic apparatus of similar design to that employed in Example 1 and was sonicated at 20 kHz for 10 seconds to generate seed crystals (ultrasonically generated crystals). The experiment was repeated without the application of ultrasound 20 (Control, non-sonicated crystals).

Samples of the crystals were examined by SEM. Measurements were made of the size and morphology of the crystals using printed images. The results obtained by measuring 100 control crystals and 112 seed crystals are presented in Tables 1 and 2 below.

25 Generally, the crystals were thin rhomboids having two flat corners. The crystal "length" measurement was made between the flattened ends of the crystal and the "width" measurement was made between the two pointed ends of the crystal.

Table 1 - Crystal dimensions

	Control crystals	Seed crystals
Length (L)	3.3 μm	1.09 μm
Width (W)	2.6 μm	1.09 μm
Thickness	0.5 μm (approx.)	0.5 μm (approx.)
Aspect ratio (L:W)	1.27	1.00
Voids ^a	0	39%

a. Percentage of crystals having voids

5 The control crystals were generally uniform in morphology. In contrast, the seed crystals were less uniform in morphology and were divided into the classes shown in Table 2.

Table 2 - Crystal Morphology

10

Morphology Class	% in Class	Length (μm)	Width (μm)
Rhomboids	54	1.06	1.05
Rhomboids having voids	39	1.04	1.01
Six sided structure	3.5		
Others	3.5		

Example 6

The following formulated brines were employed in the tests described below:

Brine A : concentration of calcium ions (Ca^{2+}) = 0.04M, pH 5

15 Brine B : concentration of bicarbonate ions (HCO_3^-) = 0.08M, pH 7

Brines A and B were both allowed to reach complete saturation with CO_2 before the pH of each brine was recorded and adjusted, if necessary, with HCl or NaOH.

Test 1

A high pressure and high temperature (HPHT) tube blocking rig was connected to a HPHT mixing 'T' piece. The mixing 'T' piece (having a first inlet, a second inlet and an outlet) was fitted with an ultrasonic horn (3/4" tip, 550W maximum output). The first and second inlets of the mixing 'T' piece were connected to a first liquid feed line and a second liquid feed line respectively while the outlet was connected to a one metre 1/16" blocking tube. A back pressure regulator (BPR) having an in-line filter was positioned at the exit of the blocking tube and maintained the pressure in the mixing 'T' piece and in the blocking tube at 200 bar.

The HPHT tube blocking rig was first primed to a pressure of 200 bar using distilled water. Distilled water was then allowed to flow through the first liquid feed line and second liquid feed line at a rate of 2.5 ml/min (both lines) until the water in the mixing 'T' piece had reached an equilibration temperature of 90°C. The feed to the first and second liquid feed lines was then switched to Brines A and B respectively (the flow rate through both lines being 2.5 ml/min). Brines A and B were mixed in the mixing 'T' piece to give a slurry of calcite crystals. The slurry then passed through the outlet of the 'T' piece into the blocking tube. The time taken to block the 1/16" blocking tube (after switching to Brines A and B) was 45 minutes. Samples were collected 40mins after initiation of the flow of Brines A and B (downstream of the in-line filter) and were immediately further filtered for SEM analysis (Control; non-sonicated crystals). Since the samples were collected downstream of the in-line filter, only a small number of crystals were collected. SEM analysis of the calcium carbonate crystals showed that the crystals had a size of 10 μ m (or less) with a flower-like morphology (Figure 7).

Test 2

The procedure outlined above was repeated except that the ultrasonic horn was activated to 10% of its total output capability. The time taken for the 1/16" tube to block was 2 hours. Treated samples were collected after 1 hour for SEM analysis (ultrasonically generated seed crystals). SEM analysis of the ultrasonically generated crystals showed small rounded crystals, roughly 2 μ m in size (Figure 8).

Tests 1 and 2 show that calcium carbonate morphology is influenced by ultrasound applied during the crystal growth period. Crystals generated in Test 2 (using ultrasound) were rounded and much smaller than those grown without ultrasound. In

addition, tube blocking time was extended from 45 mins to 2 hours.

Example 7

Control

A brine containing NaCl (66.1 g/l), MgCl₂.6H₂O (33.45 g/l), CaCl₂.2H₂O (55.02 g/l) was slowly mixed with seawater (having the composition of Example 1) in a ratio of 5:50. It was found that it took several minutes for crystals to begin to appear (Control).

Insonification

Brine (150 ml) contained in a 500 ml beaker was insonified using a 550W, 20 kHz probe. Seawater (150 ml) was rapidly added to the brine (whilst continuing to insonify the contents of the beaker). It was found that crystallisation occurred within seconds and the resulting mixture appeared pearlescent.

Analysis of the crystals by SEM showed that about 45% of the control crystals were sized below 1 µm whereas about 70% of the ultrasonically generated crystals were 15 sized below 1 µm.

20

25

30



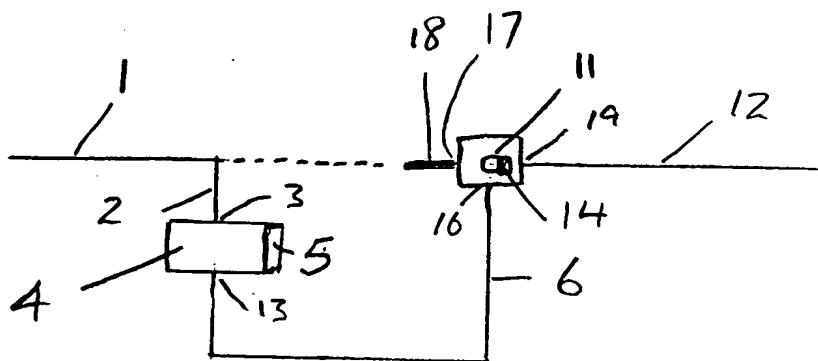


FIG 1.

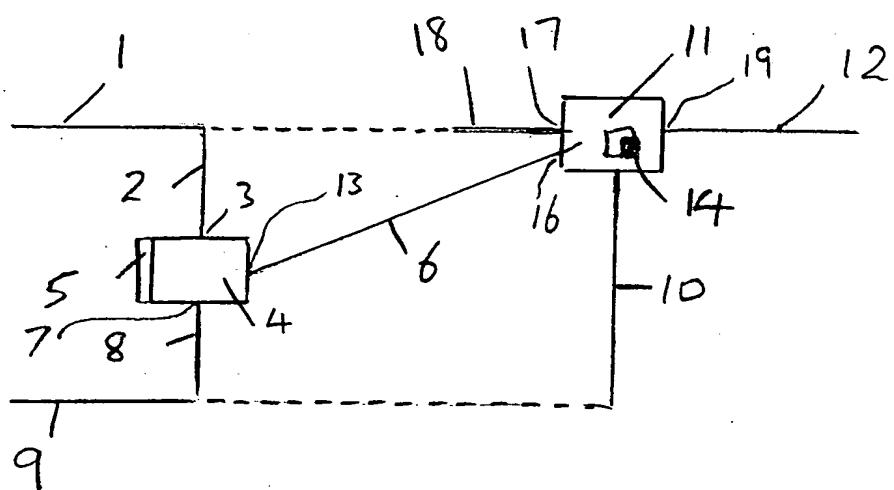


FIG 2.

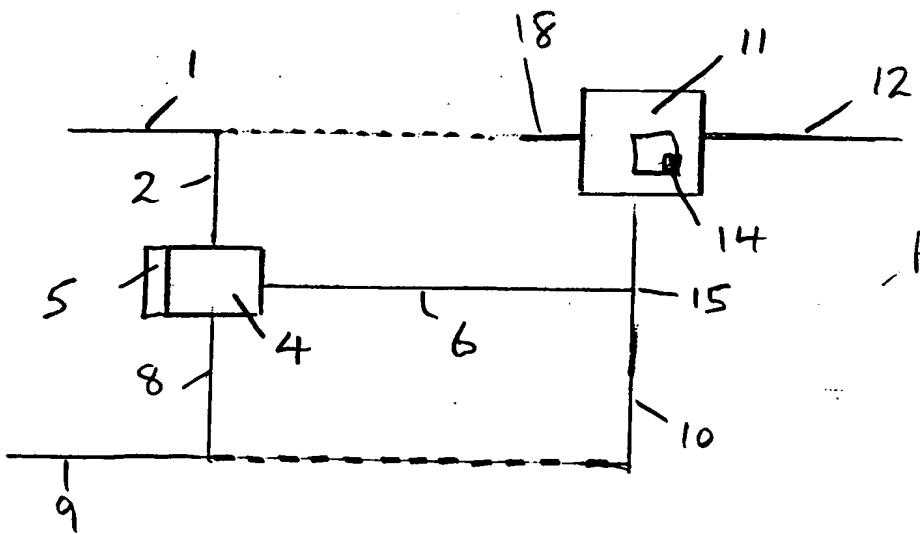


FIG 3



FIG 4

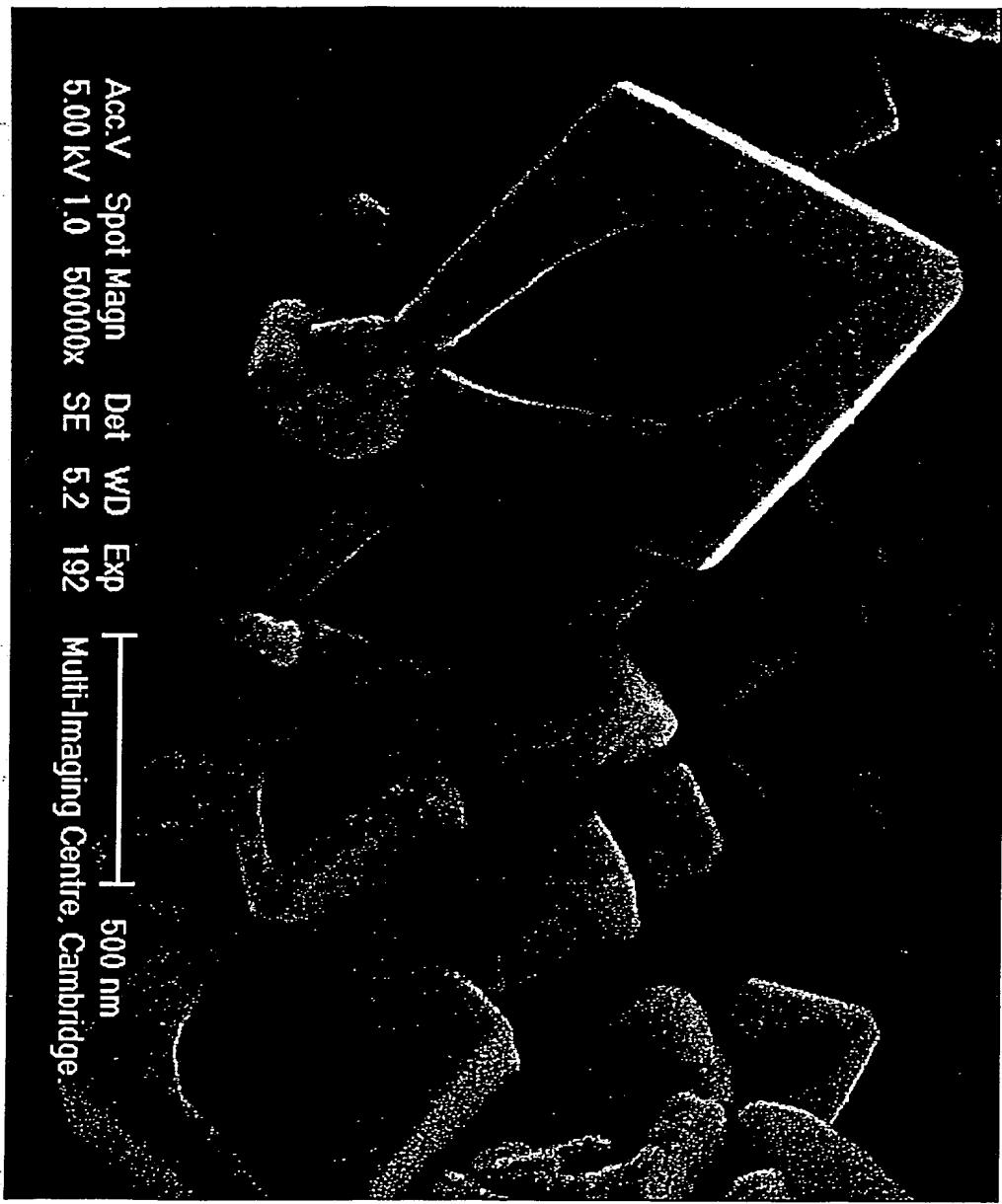
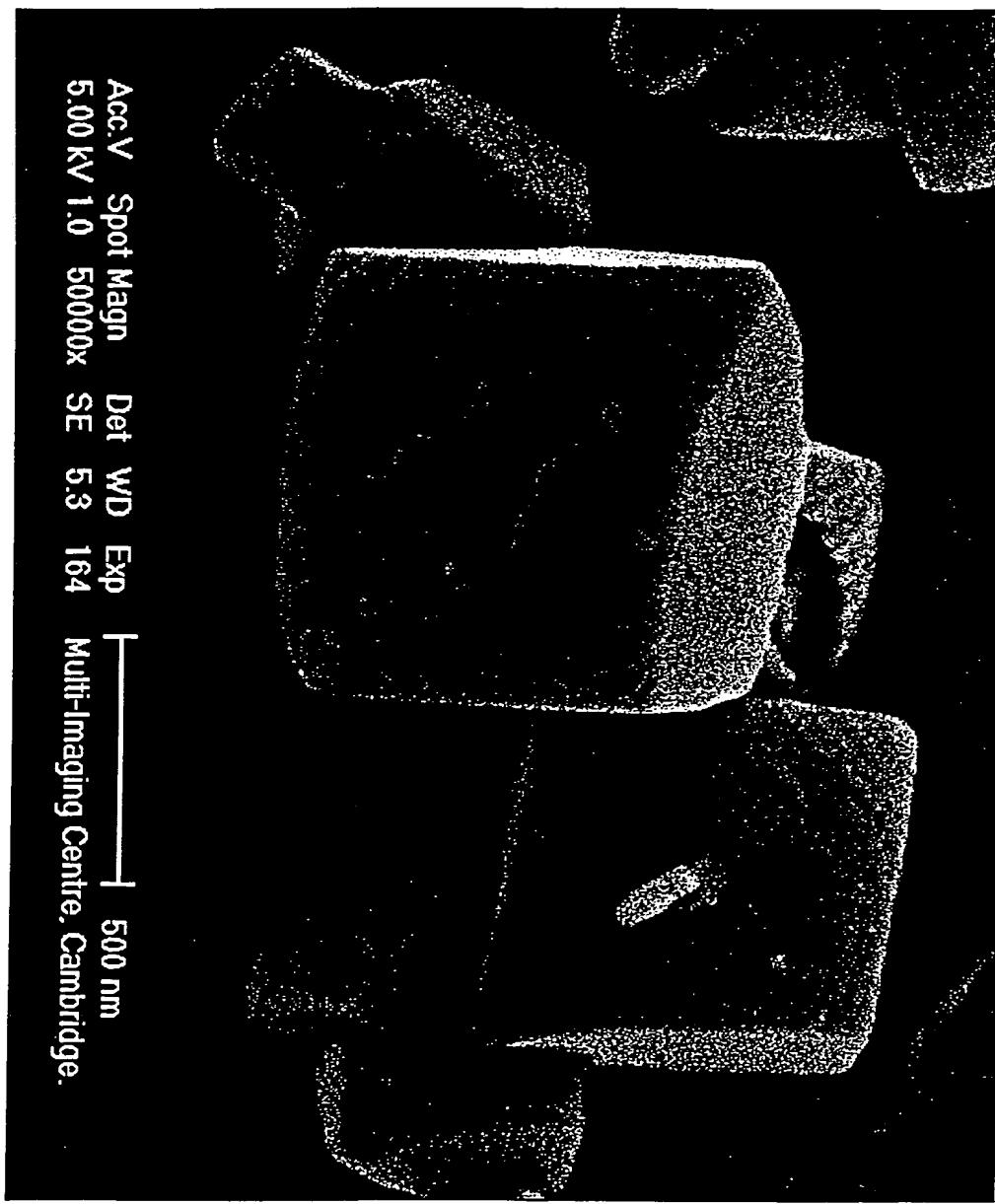




FIG 5



Acc.V Spot Magn Det WD Exp
5.00 kV 1.0 50000x SE 5.3 164
Multi-Imaging Centre, Cambridge.

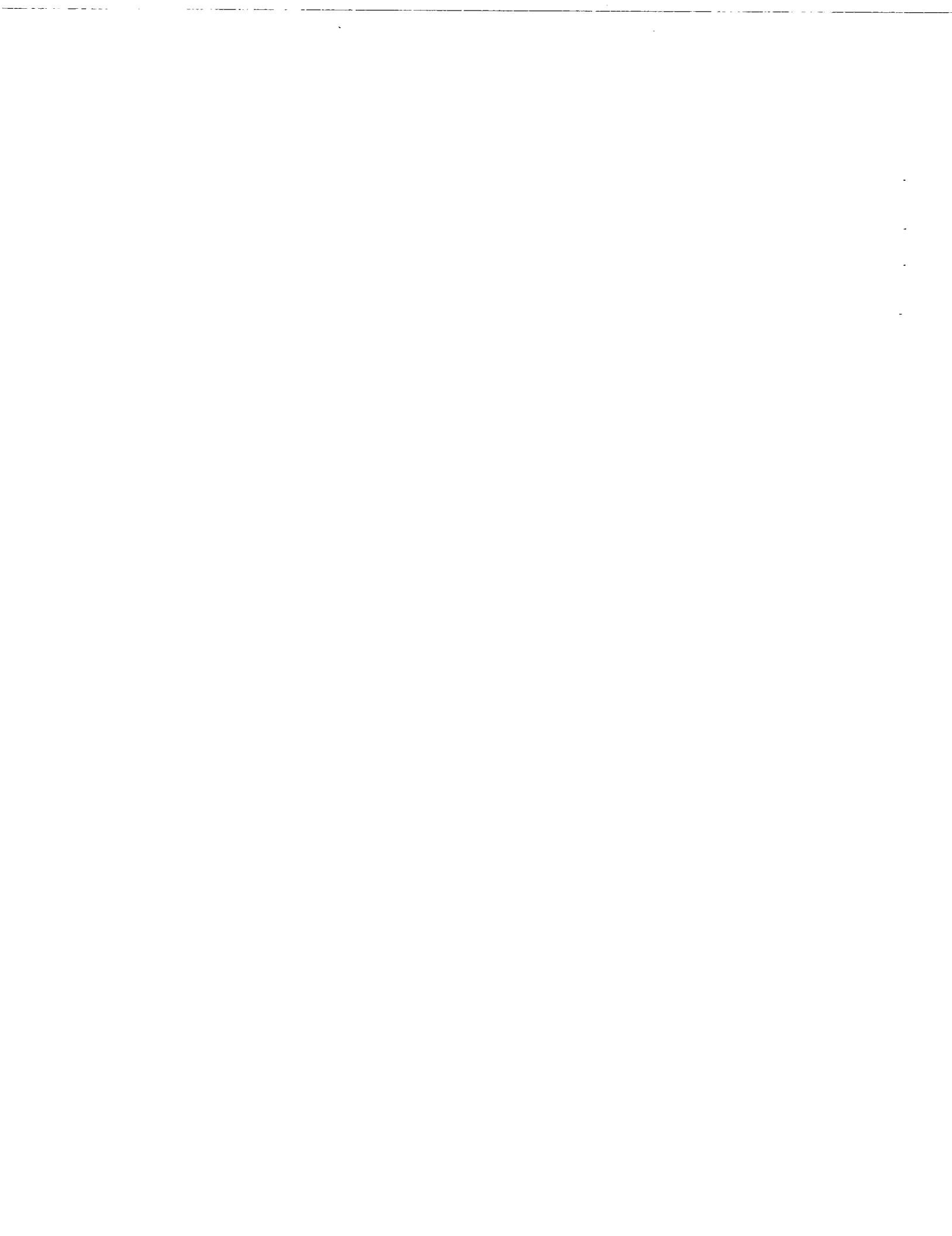


FIG 6



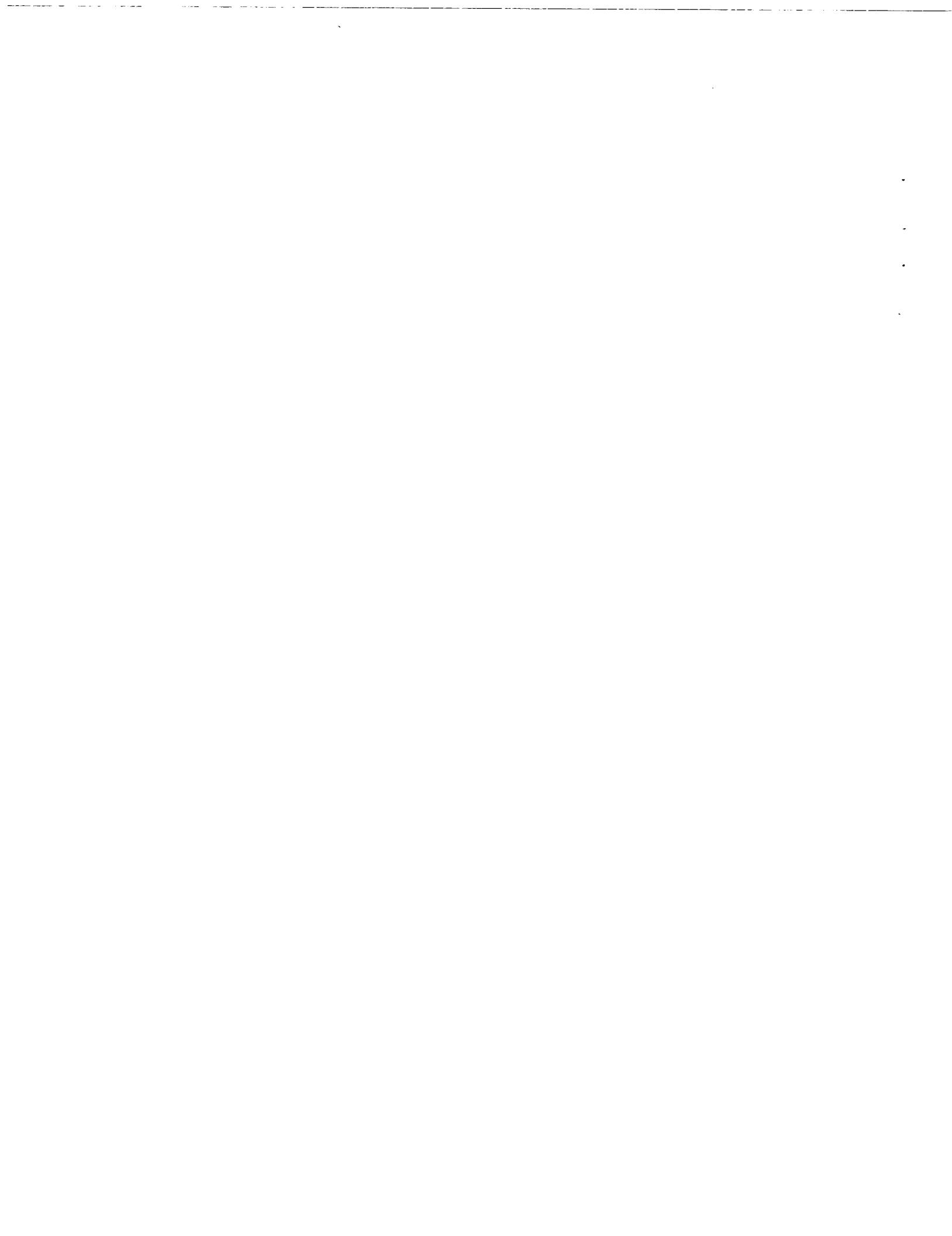
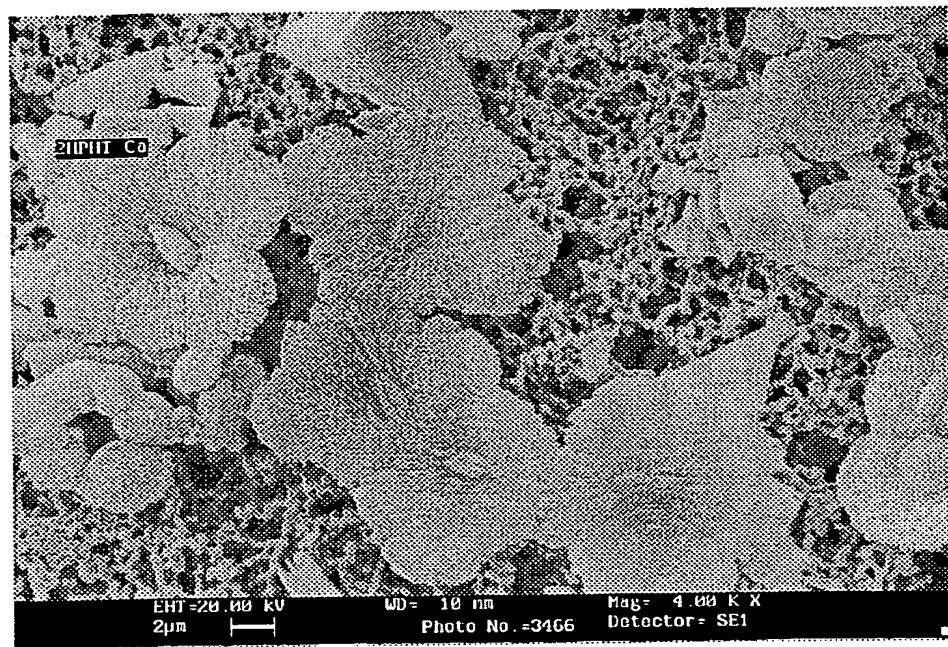


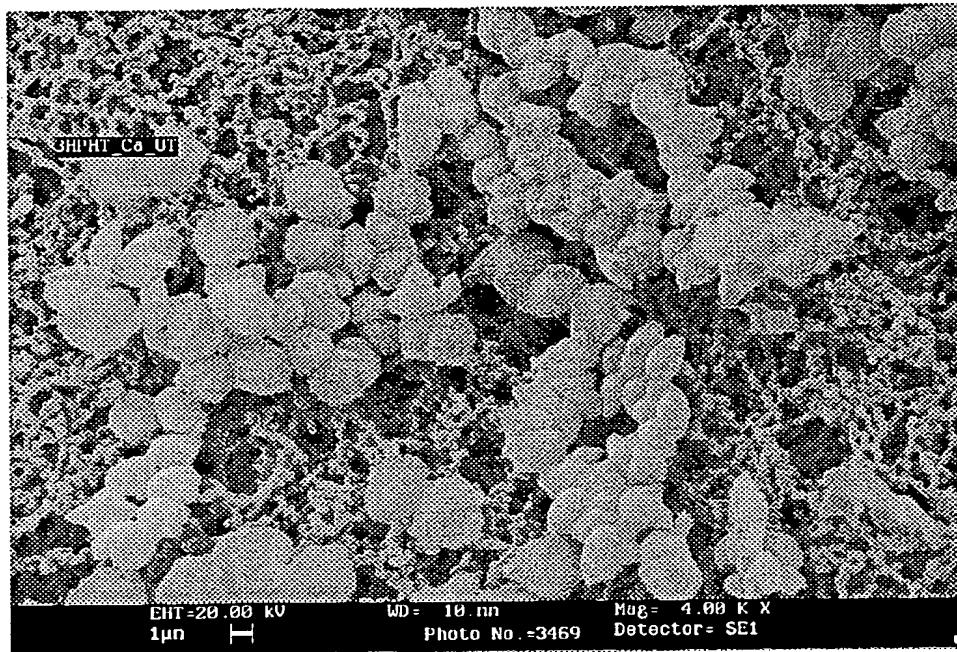
Figure 7



HPHT Tube Blocking Test 1: SEM showing Calcite Scale after 40mins; No Ultrasound



Figure 8



HPHT Tube Blocking Test 2: SEM showing Calcite Scale after 60mins ; Ultrasound (10%)

